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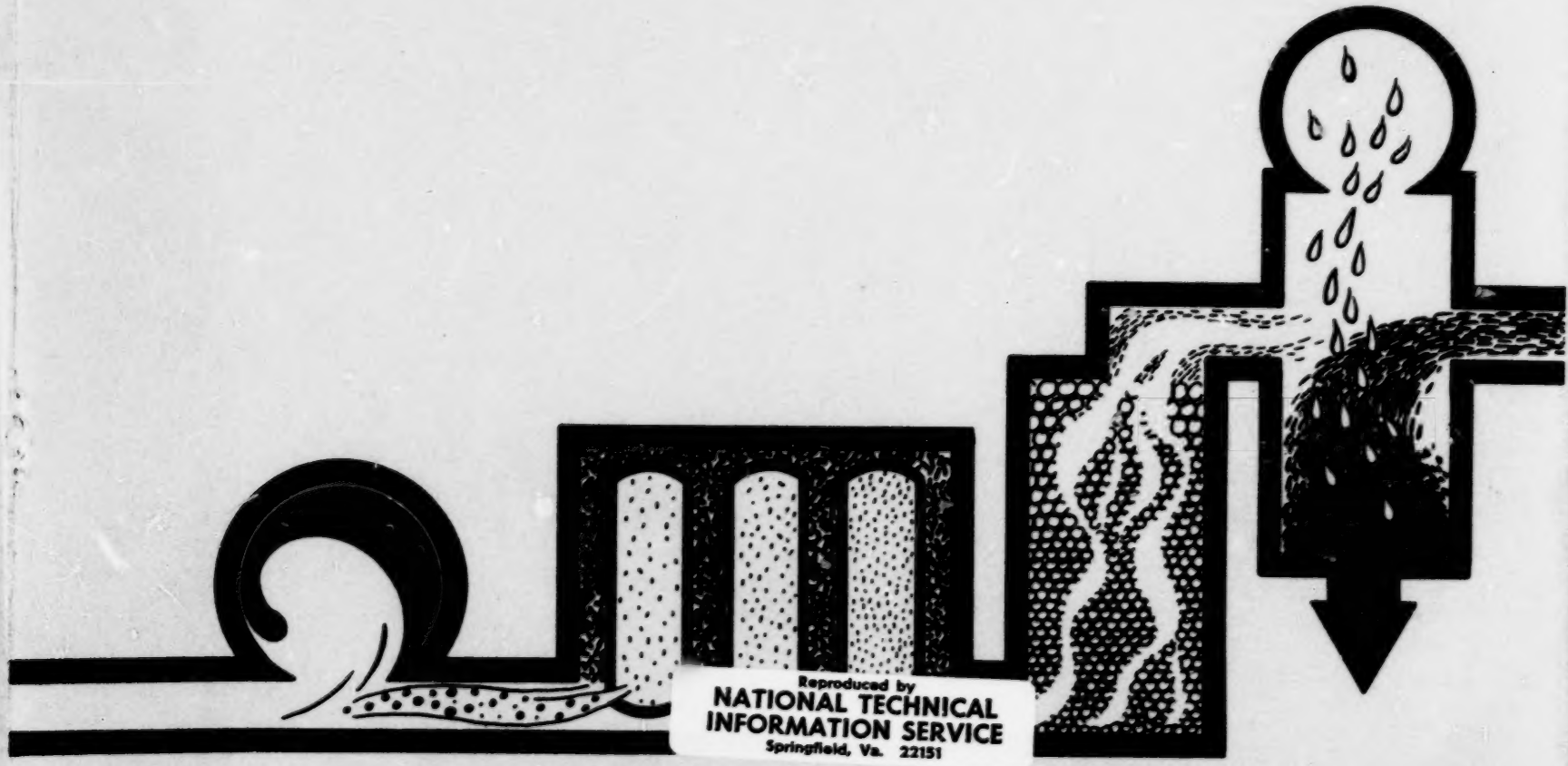
TREATMENT TECHNIQUES FOR REMOVING PHOSPHORUS FROM MUNICIPAL WASTEWATERS



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44

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TREATMENT TECHNIQUES FOR REMOVING PHOSPHORUS FROM MUNICIPAL WASTEWATERS

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27 Abstract Biological uptake, chemical precipitation of soluble phosphorus, and settling or filtration of particulate phosphorus are the major removal mechanisms used in phosphorus removal. At present, chemical precipitation is the most universally applied method. The wide variety of chemical reactions which lead to phosphorus precipitation allows much flexibility of operation to plant operators. In dealing with raw sewage, primary effluent, or secondary effluent the size of the plant , influent wastewater characteristics phosphorus discharge standard, and the types of other processes used in the treatment train must all be considered. In addition to phosphorus removal, higher levels of BOD and suspended solids removals are customarily obtained when sometype of phosphate reduction mechanism is employed. Each of the mechanisms described here have been analyzed both with respect to technological and economic feasibility. Costs ranged from 13¢/1000 gallons for two-stage lime treatment of 1 mgd to achieve 97% removal, to a potential low of $.015/1000 gallons using waste pickle liquor to achieve a reduction of 80%. (Lowry-Texas)

(WRSC - abstract)

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TREATMENT TECHNIQUES FOR REMOVING PHOSPHORUS FROM MUNICIPAL WASTEWATERS

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Presented

at
New York Water Pollution Control Association
New York, New York

Program #17010---
Environmental Protection Agency
Water Quality Office
Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio
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TABLE OF CONTENTS

I. PHOSPHORUS REMOVAL BY CONVENTIONAL TREATMENT

A. TREATMENT OF DIGESTER SUPERNATANT

B. BIOLOGICAL PHOSPHORUS REMOVAL

II. PHOSPHORUS REMOVAL BY CHEMICAL PRECIPITATION

A. IRON AND ALUMINUM SYSTEMS

1. Treatment of Raw Sewage

a. Iron Systems

2. Chemical Addition to Secondary Biological Processes

a. Activated Sludge

b. Trickling Filters

3. Tertiary Treatment with Alum

B. LIME TREATMENT

1. Raw Sewage

2. Tertiary Treatment

III. MOVING BED FILTRATION OF ALUM TREATED WASTEWATER

INTRODUCTION

A great deal of work has been and is being done to develop improved methods for removing the nutrient phosphorus from municipal wastewaters. The literature is replete with articles on the sources of phosphorus, its eutrophying effects on the water environment, the necessity for control, and the methodology of control.

The purpose of this paper is to summarize the alternative methods of removing phosphorus from municipal wastewaters. The intent is to provide perspective to those municipal officials, engineers and operators contemplating incorporation of nutrient control measures into their treatment facilities and to indicate that the necessary technology is available. Process selection will depend on specific wastewater characteristics, existing facilities, desired effluent quality, and economic considerations.

Processes considered include: conventional treatment, digester supernatant treatment, modified biological treatment, chemical addition in primary, secondary and tertiary stages of treatment, and moving bed filtration.

TABLE 2. Results Achieved by Lime Clarification of Digester Supernatant[15]

Constituent	Digester Supernatant mg/l	Treated Effluent mg/l	% Removal
Suspended Solids	1415	140	90
COD	2840	640	77.5
Total Carbon	1284	260	79.8
Ortho - PO_4 as P	44	1	97.8
Total - PO_4 as P	96	3.6	96.3

Total operating costs for digester supernatant treatment including carbon dioxide stripping, lime clarification and ammonia stripping are estimated to be about $0.30/1,000 gal. of supernatant which is equivalent to $0.01 to $0.015/1,000 gal. of total plant flow.

A comprehensive study[1] to determine the least cost solution for treating digester liquor (primary digester overflow), digester supernatant liquor, thickener overflow and a 50% mixture of primary and waste activated sludge has recently been completed. A report of the findings should be available for distribution in the near future.

B. "BIOLOGICAL" PHOSPHORUS REMOVAL

Several activated sludge plants have historically experienced high phosphate removal efficiencies. The most notable is the Rilling Road Plant at San Antonio, Texas where an average of 80% phosphate removal was experienced during 1965. There is conflicting evidence in the literature as to the mechanism of phosphorus uptake. A chemical precipitation and a biological mechanism can both be postulated to explain the observed phenomena. A summary of the two schools of thought is presented by Jenkins and Menar[10]. The first hypothesis, advocated by Sawyer, Sekikawa, et al., Hall and Engelbrecht, and Jenkins and Menar, states that biological removal of phosphate can only account for 20% - 30% of the influent phosphate with an activated sludge phosphorus content of 2% - 3% and standard substrate removal rates in the range of 0.4-1.0 lb COD removed/lb MLVSS-day. Phosphate removal in excess of that predicted by biological growth requirements is caused by chemical precipitation of calcium phosphate. Simply stated, the postulated mechanism involves:

1. Hydrolysis of condensed phosphate to orthophosphate;

2. Decreased production of CO_2 through the aerator as the organic matter is oxidized;

I. PHOSPHORUS REMOVAL BY CONVENTIONAL TREATMENT

The conventional treatment techniques of settling and biological oxidation are capable of removing some phosphorus as indicated in Table 1.

TABLE 1. Phosphate Removal by Conventional Waste Treatment Plants

Type of Treatment Plant	% Phosphorus Removal
Primary Sedimentation	5-15
Primary and Trickling Filter	20-30
Primary and Activated Sludge	30-50

Regardless of the complex internal mechanism of phosphate removal (precipitation, absorption, etc.), the actual phosphorus removal that a conventional plant can achieve will ultimately depend upon the amount of sludge permanently removed from the process stream. Since some 80% of the phosphates present in sludge are solubilized during anaerobic digestion, the higher removal efficiencies cannot be achieved unless the recycle of untreated digester supernatant is eliminated.

A. TREATMENT OF DIGESTER SUPERNATANT

Treatment of the digester supernatant stream separately can achieve effective phosphorus removal. Lime clarification and ammonia stripping have been evaluated[15] for the treatment of digester supernatant. The supernatant is first air blown to strip out CO_2 which raises the pH of 8.6 thereby reducing the lime requirements. A lime addition of 3 to 4 gm/l is then added to achieve the required operating pH of 11 to 12. At this elevated pH, the phosphorus is precipitated and the ammonia nitrogen in the clarifier effluent (375 mg/l) can be efficiently stripped in a countercurrent tower. At 20°C, approximately 275 ft^3 of air/gal. is required to achieve 90% ammonia removal. At 60°C, about 50 ft^3/gal. would be required to achieve 90% removal. However, heating the digester supernatant to reduce the air and equipment requirements is not economically justified. Removal efficiencies of the lime clarifier are shown in Table 2.

1. Specialized design of the activated sludge plant to achieve removal of phosphorus by either luxury uptake and/or physical-chemical phenomena should be avoided. Such removals should be considered a bonus when and if they occur in existing or newly constructed plants.

2. While maximum phosphorus removals (0.022 to 0.026 lbs of P/lb of COD removed) were possible at a cell residence time of 3.6 days, overall phosphorus removal was limited by plant design considerations, effluent suspended solids concentrations and phosphorus release during solids separation.

3. Total plant operating costs were estimated to be $0.48/1,000 gal., or 2 to 3 times the cost of conventional activated sludge.

4. Significant operating problems were experienced in handling the waste activated sludge which was difficult to dewater.

II. PHOSPHORUS REMOVAL BY CHEMICAL PRECIPITATION

The current state-of-the-art of phosphorus removal technology indicates that chemical precipitation is the most economical method of removing phosphorus from municipal wastewater. Alternatives which the design engineer must consider include the choice of chemicals (iron, aluminum or lime) and the point of chemical addition (primary, secondary or tertiary). The point at which to add the chemicals is dependent to a great extent on the other unit processes being utilized in the treatment train. Phosphorus removal is not an isolated design problem capable of solution through independent considerations; it requires an integrated solution consistent with all other treatment requirements.

The choice of chemical and point of addition depends on several factors shown in Table 4. The significance of each will become apparent in the detailed discussions of each chemical system.

TABLE 4. Factors Affecting Choice of Chemical and Point of Addition for Phosphorus Removal

1. Influent Phosphorus Level
2. Effluent Discharge Standard
3. Wastewater Characteristics (Alkalinity, Etc.)
4. Plant Size
5. Chemical Costs Including Transportation
6. Sludge Handling Facilities
7. Ultimate Disposal Alternatives
8. Other Processes Utilized

3. An increase in pH occurs due to the reduced CO_2 generation and removal of CO_2 by aeration;

4. Localized pH conditions exist which are favorable for the precipitation of calcium phosphate.

The second point of view, advocated by Levin and Shapiro, Borchardt and Azard, and Connell and Vacker indicates that under certain conditions, activated sludge is capable of removing more phosphate than it requires for growth. This biological uptake of excess phosphate has been termed "luxury uptake." It is thought by these authors that the percentage of phosphate incorporated into the biological sludge is affected by the growth rate of the organisms and certain process operating parameters such as the organic loading, mixed liquor suspended solids concentration (MLSS), aeration rate, and mixed liquor dissolved oxygen (D.O.) concentration. The design and operating criteria reported in the literature to achieve luxury uptake of phosphorus are shown in Table 3.[14]

TABLE 3. Conditions for "Luxury Uptake" as Reported in the Literature[14]

DO - mg/l	> 2.0
Air Supply - ft^3/gal.	3-7
Hydraulic Detention Time - Hours	3-6
Organic Loading lb BOD/lb MLSS day	0.4-0.5
MLSS - mg/l	2500-4000
Sludge Detention Time for Solids Separation - Hours	< 1.0

Investigations are currently being conducted to further elucidate the mechanisms of phosphate removal by activated sludge treatment. A 1-mgd plant, specifically designed and operated for maximum biological uptake of phosphorus, has been constructed and operated through a cooperative effort between the Greater Manassas Sanitary District, Prince William County, Virginia and the Federal Water Quality Administration. The plant treatment facilities consist of a first-stage aerator, flotation unit, second-stage aerator, final clarifier, chlorine contact tank, digesters, supernatant treatment facilities and sand drying beds. A recent report[14] on the operation of this plant concluded:

Iron Systems

Performance results from several full-scale plants with chemical addition in the primary are shown in Table 6. The chemical systems and dosing levels used are shown in Table 7. Overall removal of suspended solids, biochemical oxygen demand and phosphorus was significantly improved. Since these removals were attained in existing facilities, higher removal efficiencies can be expected with plants especially designed for chemical treatment of raw sewage.

It is interesting to note that both forms of waste pickle liquor, ferrous chloride (9% Fe at Mentor) and ferrous sulfate (6%-9% Fe at Texas City), were successfully used for phosphorus removal. When available within reasonable hauling distances, these materials are an inexpensive source of iron ($0.015/lb of Fe at Texas City and $0.02/lb of Fe at Mentor, Ohio).

Several features of the Texas City, Texas operation and performance are significantly different from the other plants mentioned. Ferrous sulfate was added to the raw sewage without a base or polyelectrolyte. Very little phosphorus (0.03 mg/l as P) was removed by primary treatment. The bulk of the phosphorus (4.7 mg/l as P) was removed in the aerator and final settler to yield an overall phosphorus removal efficiency of 81% with an effluent concentration of 1.1 mg/l. The ferrous iron was oxidized to the ferric iron in the aerator, thereby eliminating the required addition of a base such as $Ca(OH)_2$ or NaOH. The aerator served as an excellent collector of the iron phosphate precipitate, which can be attributed to the large floc mass available in the aerator to absorb the precipitate, and the presence of naturally occurring polymeric material to aid flocculation. A ferrous system can be used to attain phosphorus removal in an activated sludge plant without the use of a base or polyelectrolyte. However, if a base and polyelectrolyte were used with the ferrous system one could expect to remove increasing amounts of phosphorus, suspended solids and BOD in the primary thereby reducing the load on the secondary facilities. Also, a greater portion of the phosphorus removed in the primary would be chemically bound, thereby reducing the phosphorus concentration in the digester supernatant return.

Experience at Mentor, Ohio indicates that addition of a base and polyelectrolyte are necessary to efficiently remove phosphorus from a primary plant with a ferrous system as shown in Table 8.[3]

These data indicate that the base is more important than the polymer. (Compare treatment conditions 4 and 5). The function of the base is not well understood; it could be an olation reaction in which the hydroxyl ions bridge between the iron molecules effecting a certain degree of polymerization.

A. IRON AND ALUMINUM SYSTEMS

1. Treatment of Raw Sewage

The alternative chemical systems for phosphorus removal in the primary are shown in Table 5. The iron and aluminum systems are discussed together because of the similarity in chemistry, dosing requirements, design considerations and performance. A discussion of lime precipitation in primary and tertiary treatment applications is deferred for separate consideration.

Phosphorus removal should be thought of as a two-step operation: precipitation of the soluble phosphorus and removal of the insoluble phosphorus.

With the iron and aluminum systems, the primary coagulant is added first at a dose of 1.25 to 1.75 mole of metal ion per mole of soluble phosphorus to precipitate the soluble phosphorus. The dosing is therefore proportional to both the influent soluble phosphorus concentration and flow.

With the ferrous system, a base, either $Ca(OH)_2$ or NaOH must be added to achieve optimum flocculation in the primary. Next the insoluble phosphorus is removed by flocculation with anionic polymers and settled or filtered with a device such as the Moving Bed Filter (discussed in detail later).

Sufficient time (0-5 min) should be provided between dosing of the primary coagulant and base if necessary, and dosing of the organic polyelectrolyte to insure completion of the precipitation reactions. This can best be determined by preliminary jar testing. If there is insufficient detention time or inadequate mixing conditions in the influent sewer, separate mixing and flocculation facilities will have to be provided.

TABLE 5. Alternative Chemical Systems for Phosphorus Removal in the Primary

A.	Iron:	
	Ferrous Chloride or Sulfate	Base Without Polymer
	Commercial or Waste Pickle Liquor	Lime or Sodium Hydroxide
	Ferric Chloride or Sulfate	Without Polymer
B.	Aluminum:	
	Alum or Aluminate	Without Polymer
C.	Lime:	Without Additives
	1 or 2 Stage	

TABLE 8. Results of Selected Chemical Treatment in Primary Utilizing Waste Pickle Liquor[3] - Mentor, Ohio

Treatment Conditions	Flow MGD	% Removal			
		Suspended Solids	BOD	COD	Total Phosphorus
1. Polymer - 0.5 PPM	2.4	37	24	44	9.5
2. Lime - 67 PPM	2.4	48	15	33	46
3. Iron - 50 PPM	3.8	13	30	29	40
4. Iron - 50 PPM Polymer - 0.5 PPM	4.6	5.3	29	34	42
5. Iron - 43 PPM Lime - 55 PPM	4.6	58	62	63	76
6. Iron - 43 PPM Lime - 66 PPM Polymer - .4 PPM	4.0	74	59		83.5

The liquid handling aspects of phosphorus removal in the primary clarifier are relatively straight forward and well quantified. Sludge handling considerations and other plant operations are also significant, but the current data is less definitive. Probably the most quantitative data available are the results at Benton Harbor[11] which are shown in Table 9.

TABLE 9. Plant Data at Benton Harbor Using Ferric Chloride[11]

	No Chemical Addition	Chemical Addition	
		Recycle to Primary*	No Recycle*
Primary Clarification			
Volume Pumped, Gal/Day	53,200	51,600	46,100
Percent Solids	3.80	4.29	4.82
Percent Volatile	64	63	60
Mixed Liquor Data			
Suspended Solids, mg/l	2500	2700	2400
Sludge Volume Index	85	78	64
Dissolved Oxygen, mg/l	4.8	5.9	6.6
Air Applied, cfm	4480	4940	4710
Digester Operation			
Gas Production - ft^3	37,800	44,400	40,800
Gas Production - ft^3/lb of solids	3.48	3.82	3.67

* Recycle refers to Waste Activated Sludge

TABLE 6. Phosphorus Removal at Full-Scale Plants Adding Chemicals in the Primary

Type of Plant	Average Influent Phosphorus mg/l	Fe/P mole ratio	% Removal - Total Plant			
			Suspended Solids	BOD	Total Phosphorus Range,	Average
Primary:						
Grayling	15.5	1.1-1.8	78(61)*	58(40)	60-80	72
Mentor	15.7	1.4	74	59		83.5
Trickling Filter:						
Lake Odessa	--	--	89(78)	82(62)	75-95	82
Activated Sludge:						
Benton Harbor	7.5	1.55	92.5[72.5]**	--		90.9[65.3]
Texas City	6.2	1.7	--	84.7***	72-94	87.2

*( ) Without Chemical Addition
**[ ] Removal Efficiency Across the Primary
***COD

TABLE 7. Chemical Systems and Dosing Levels Used at Full-Scale Plants for Phosphorus Removal

Location	Chemical	Dose
Grayling, Mich.[25] & Lake Odessa, Mich.	$FeCl_2$ as Fe	15-25 mg/l
	$NaOH_2$* as $CaCO_3$	30-50 mg/l
	A-23*	0.3-0.5 mg/l
Benton Harbor, Mich.[11]	$FeCl_3$ as Fe	21.0 mg/l
	A-23	0.3 mg/l
Mentor, Ohio[3]	Waste Pickle Liquor, $FeCl_2$ as Fe	43 mg/l
	Lime*	66 mg/l
	A-23*	.4 mg/l
Texas City, Texas[23]	Waste Pickle Liquor, $FeSO_4$ as Fe	19 mg/l

*A-23 Anionic Polyelectrolyte - Product of the Dow Chemical Company**
**Mention of a proprietary product does not constitute an endorsement or recommendation by the Federal Government.

The chemical costs at Mentor, Ohio, utilizing waste pickle liquor, are estimated to be $0.023/1,000 gal[3]. An additional cost of $0.01/1,000 gal. is required to handle the excess sludge through digestion and vacuum filtration.

2. Chemical Addition to Secondary Biological Processes

a. Activated Sludge. The pioneering work in this area was conducted by E. A. Thomas and more recently by Barth and Ettinger[4]. For their studies various chemicals were added to the aerator of a 100-gpd activated sludge plant. Results are shown in Table 10.

TABLE 10. Phosphorus Removals Obtained by Mineral Addtion to the Aerator[4]

Chemical	Dose mg/l	Phosphorus Removal %
None		40
Calcium	150	64
Calcium + Fluoride	150 6	75
Magnesium	20	50
Ferric Iron	15	75*
Aluminum (as Alum)	20	70*
Aluminum (as Alum) Calcium	30 20	90
Aluminum (as Sodium Aluminate)	5	74-94
Aluminum (as Sodium Aluminate)	10	90-98

*Turbid effluent

The study at Benton Harbor was conducted in three stages, a baseline period with no chemical addition, a second period with the addition of ferric chloride and polymer with wasting of the activated sludge to the primary and a third period in which there was no wasting to the primary. Benton Harbor utilizes the "Kraus Process" which consists of returning a reaerated portion of the digested solids and waste activated solids to the primary. Chemical addition increased the solids concentration of the primary sludge from 3.8% to 4.3%. When wasting activated sludge to the primary was discontinued, the solids concentration increased to 4.8%. The chemical addition and removals accomplished in the primary benefited the operation of the "Kraus Type" activated sludge treatment. Dissolved oxygen in the aeration tanks increased and the settleability of the activated sludge improved with the sludge volume index decreasing from 85 to 78 and 64 respectively. No quantitative data are available on the effect of various degrees of chemical treatment in the primary on the performance of the conventional activated sludge process. A full-scale study to evaluate these effects at Grand Rapids, Michigan has been supported by an FWQA grant. A short-term study has been carried out at Pontiac, Michigan[18]. Preliminary results indicate that satisfactory performance of the biological system was maintained utilizing 75% of the design capacity.

Digester operations proceeded normally at Texas City, Mentor and at Benton Harbor where gas production increased from 3.48 to 3.82 ft^3/lb total volatile solids. The soluble phosphate concentration in the digester supernatant return was very low.

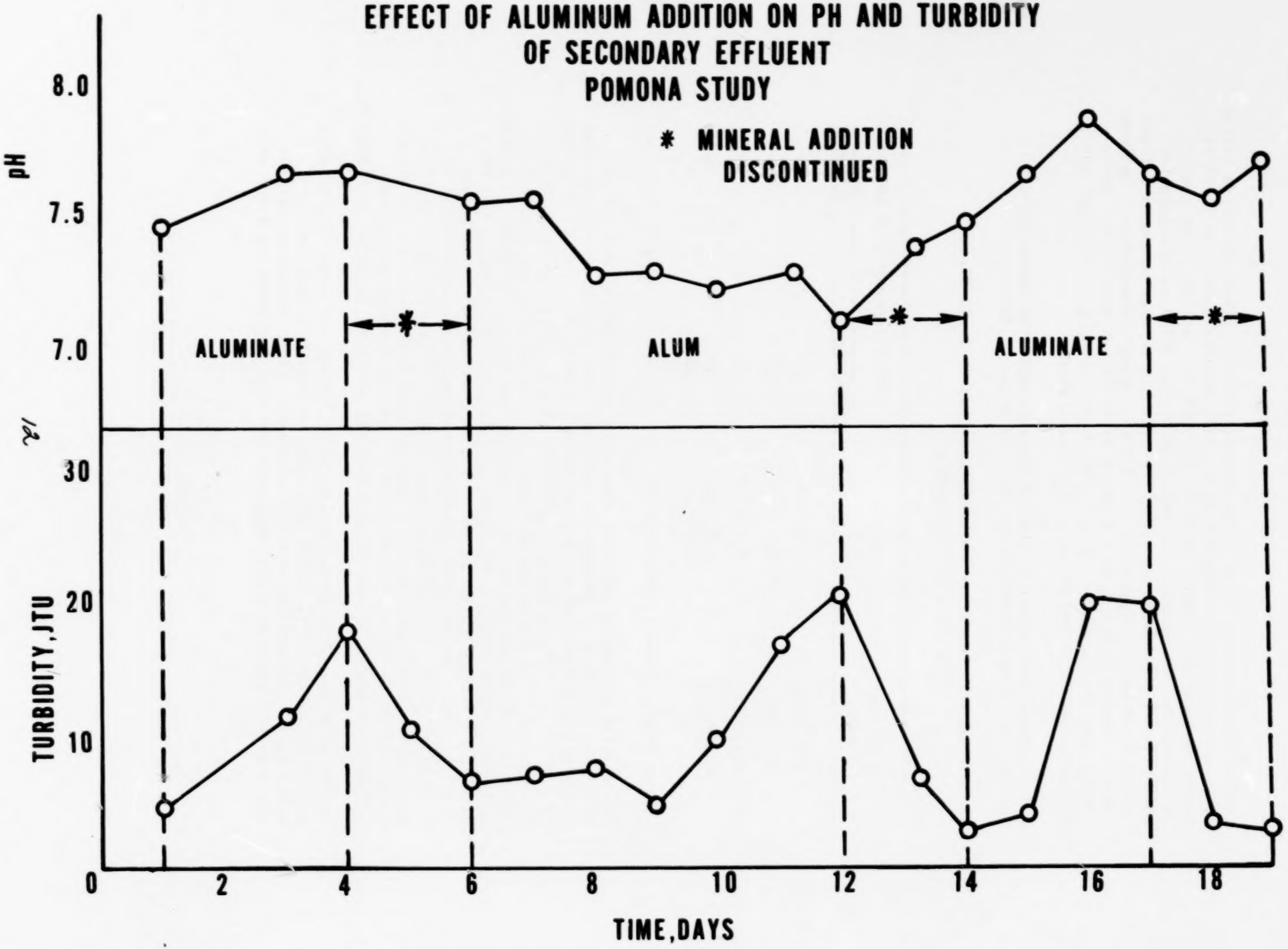
Chemical requirements for sludge conditioning at plants utilizing ferric chloride and lime such as Pontiac, Michigan (activated sludge) and Wyoming, Michigan (trickling filter) were unaffected by the iron treatment. Plants utilizing polymers for sludge conditioning such as Cleveland Westerly required additional anionic polymer to neutralize the positive charges of the iron floc[18]. Vacuum filter yields were also comparable with and without the iron treatment. There is of course an increase of about 20% in the total pounds of solids that must be handled in a primary plant. In an activated sludge plant this would be offset in part by a reduction in the pounds of waste activated sludge produced.

Cost Estimates

Operating costs of chemical treatment in the primary depend on the choice of chemical system, chemical costs, transportation costs, and handling costs for the additional inorganic sludge.

Capital costs will include chemical storage facilities, slurry and feeding systems and, where necessary, additional mixing and flocculation facilities. Total operating costs have been estimated for facilities like Lake Odessa and Grayling, Michigan to range from a possible low of $0.01/1,000 gal. to $0.05/1,000 gal[25].

FIGURE 1
EFFECT OF ALUMINUM ADDITION ON PH AND TURBIDITY
OF SECONDARY EFFLUENT
POMONA STUDY



Sodium aluminate was found to be superior to the other additives tested in terms of phosphorus removal efficiency and the fact that it eliminated the need for adding sulfate, chloride or calcium if pH control is necessary. In general the addition of 1.4 moles of aluminum for each mole of phosphorus entering the aeration chamber produced a final effluent containing approximately 0.5 to 1.0 mg/l phosphorus. Optimum dosages ranged from 1.2 to 1.6 moles of Al^{+++} per mole of P. Overdosing was detrimental to plant performance causing an increase in effluent turbidity and phosphorus concentration.

A full-scale evaluation (2 mgd) of mineral addition conducted at Pomona, California produced the results shown in Table 11.

TABLE 11. Results of Mineral Addition to 2-mgd Plant at Pomona, California

Aluminum Form	Ratio Al:P	Overall Phosphorus Removal %	
		Unfiltered	Filtered
$NaAl(OH)_4$	1:1	78	85
$NaAl(OH)_4$	1.5:1	85	94
$NaAl(OH)_4$	2:1	90	96
$Al_2(SO_4)_3$	1:1	80	83
	1.4:1	90	95

The results at Pomona indicate that alum was slightly superior to aluminate in terms of phosphorus removal. One problem resulting from the mineral addition was a deterioration of effluent quality in terms of turbidity. The changes in effluent pH and turbidity as a function of aluminum dose are shown in Figure 1. The addition of either alum or sodium aluminate raised the effluent turbidity from about 4 Jackson Turbidity Units (J.T.U.) to about 20 J.T.U. This turbidity can be attributed to the change in pH beyond the optimum pH for aluminum flocculation. The effluent turbidity returned to normal within two days after the mineral addition was stopped. The turbidity problem was solved by the addition of 2 mg/l of polyelectrolyte to the mixed liquor prior to final clarification. The improvement in effluent turbidity effected by the polyelectrolyte addition is shown in Figure 2.

Before mineral addition was initiated at Pomona the mixed liquor suspended solids averaged 1,800 mg/l and the return sludge averaged 4,000 mg/l. The solids were 75% volatile. After aluminum addition the MLSS increased to 3,000 mg/l and the RSSS increased to 8,200 mg/l.

The solids were 61% volatile. Because of this significant change in the percent of volatile solids in the return sludge and mixed liquor solids, it is imperative that the amount of sludge wasting be accurately controlled. If this is not done there is a distinct possibility that not enough active bacterial solids will be retained to maintain the treatment efficiency of the biological process. This is particularly significant in the extended aeration type of operation where the rates of cell growth are low.

The pilot plant results of Barth, et al.[4], indicated that the mixed sludge produced with mineral addition had superior settling characteristics (SDI=1.3) compared to the biological sludge (SDI=0.5). Digester operation and gas production were reported to be normal. The phosphorus content of digester supernatant was reduced from 50 - 100 mg/l to 10 mg/l as P indicating that the phosphorus remained insoluble through anaerobic digestion.

b. Trickling Filters. Direct dosing of aluminate to a trickling filter was evaluated at Fairborn Ohio[5]. The results are shown in Table 12. This approach cannot be recommended where high phosphorus removal efficiency is required.

TABLE 12. Results of Direct Dosing of Aluminate to a Trickling Filter[5]

Unit efficiency - Primary effluent to final effluent

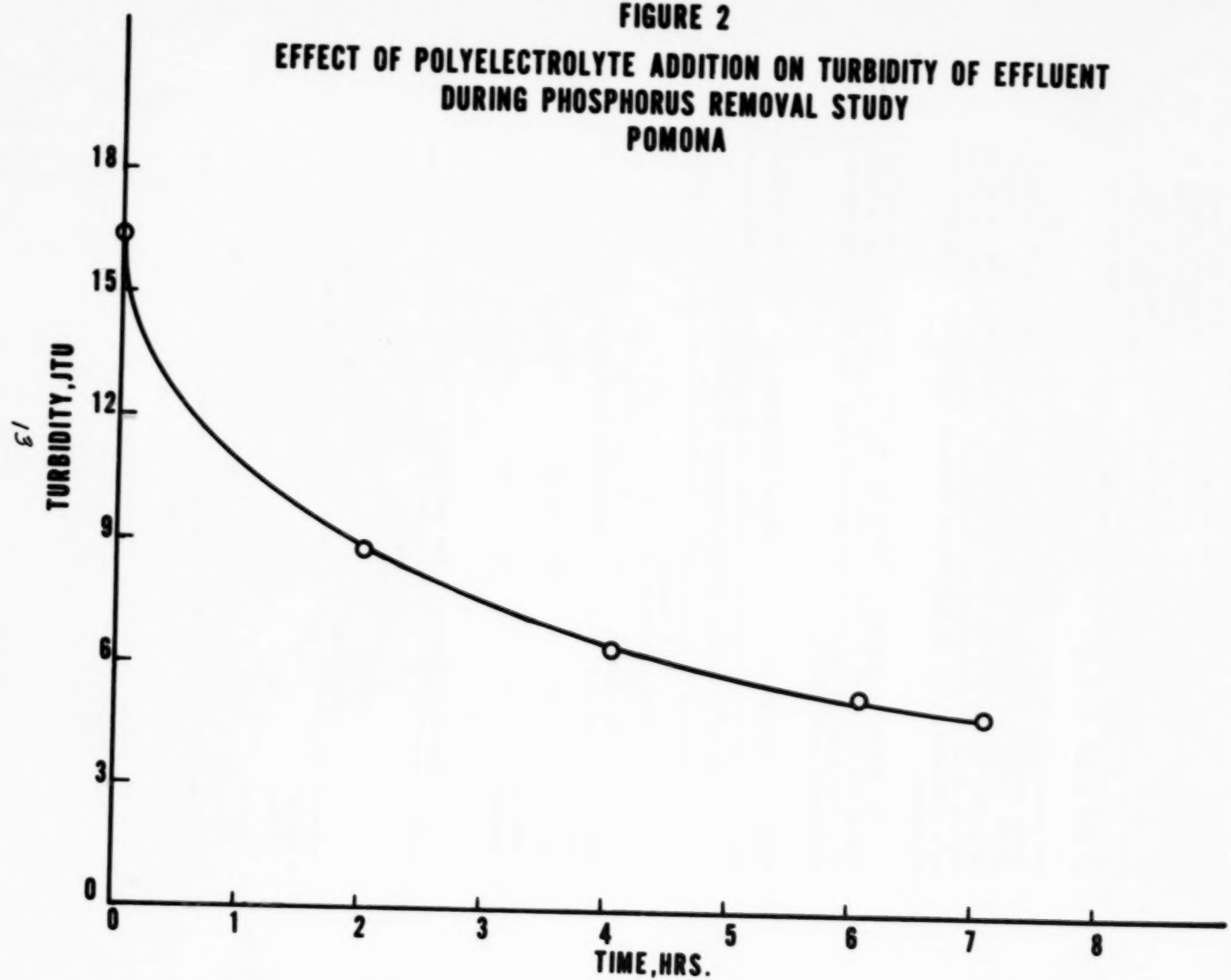
	% Removal				
	Total Phosphorus	COD	S. S.	pH	Al:P
Dosed Filter	63	74	51	7.9	1:1
Control Filter	13	75	51	7.8	---

Overall efficiency - Raw wastewater to final effluent

	% Removal				
	Total Phosphorus	COD	S.S.	pH	Al:P
Dosed Filter	64	83	84	7.9	1:1
Control Filter	17	83	85	7.8	---

FIGURE 2

EFFECT OF POLYELECTROLYTE ADDITION ON TURBIDITY OF EFFLUENT
DURING PHOSPHORUS REMOVAL STUDY
POMONA



Tertiary alum clarification, filtration and granular carbon adsorption is being used to renovate 400-gpm of secondary effluent from the Nassau County, New York Bay Park Plant. Alum was chosen to minimize post precipitation problems in the injection well and maintain chemical equilibrium between the renovated water and the water in the aquifer. Unlike lime sludges, alum sludges cannot be recovered and reused. Although several recovery schemes are being investigated for alum recovery, none has yet proven to be practical.

Alternative methods of alum sludge dewatering might include natural freezing[9] where appropriate, and rotary precoat vacuum filtration.

B. LIME TREATMENT

The chemistry of lime treatment is entirely different from the chemistry of the iron and alum systems. When slaked lime, $Ca(OH)_2$, is added to the wastewater, it reacts with the bicarbonate alkalinity precipitating $CaCO_3$. Calcium ions also react with the orthophosphate to precipitate hydroxylapatite $Ca_5(OH)(PO_4)_3$, the only stable calcium phosphate phase in the alkaline pH range. The precipitation of $Mg(OH)_2$ begins around pH 10 and is essentially complete at pH 12. A simplified representation of the reactions that occur are as follows:

Precipitation

$$5\ Ca^{++} + 7\ OH^- + 3\ H_2PO_4^- = Ca_5OH(PO_4)_3(S) + 6\ H_2O$$

$$Ca^{++} + HCO_3^- = CaCO_3(S) + H_2O$$

$$Mg^{++} + 2\ OH^- = Mg(OH)_2(S)$$

Recarbonation

$$Ca^{++} + 2\ OH^- + CO_2 + H_2O = CaCO_3(S) + 2\ H_2O$$

$$Mg(OH)_2 + 2\ CO_2 = Mg^{++} + 2\ HCO_3$$

Recalcination

$$CaCO_3 + HEAT = CaO + CO_2$$

$$Mg(OH)_2 + HEAT = MgO + H_2O$$

Cost Estimates

Principal operating costs for chemical addition to the aerator will be the cost of chemicals. Alum at $0.24/lb* or aluminate at $0.35/lb* are quite comparable in performance and can be used together for precise pH control if necessary. To achieve 90% phosphorus removal with a wastewater containing 10 mg/l of phosphorus in the primary effluent, the alum costs would be $0.024/1,000 gal. at a mole ratio of 1.4:1 Al/P. The only additional costs are the amortized cost of the chemical feed system and the operating costs associated with handling the increased quantity of sludge. Total operating and maintenance costs are estimated to be $0.036/1,000 gal.

3. Tertiary Treatment with Alum

Excellent phosphorus removal can be obtained by tertiary alum clarification. Results of studies at the FWQA-Lebanon Pilot Plant are shown in Table 13.

TABLE 13. Results of Tertiary Alum Treatment at Lebanon, Ohio

Process Stream	Suspended Solids, mg/l	Phosphate mg/l $PO_4^{\equiv}$	Turbidity J.T.U.
Secondary Effluent	45.6	22.4	12.2
Settled Alum-Treated Effluent	11.0(76%)**	2.2(90%)**	1.5(88%)**
Filtered Product	1.3(97%)**	0.9(96%)**	0.5(96%)**

Operating Conditions:

Overflow rate:	700 gpd/ft^2	Effective size of coal:	1.325 mm
Alum dose:	82 mg/l	Effective size of sand:	.45 mm
Aluminate dose:	68 mg/l	Length of run:	25 hrs.
Silica dose:	3 mg/l	Alum sludge concentration:	1.2% by wgt.
Filtration rate:	3 gpm/ft^2	Solids concentration in backwash water:	475 mg/l

**Percent Removal

*cost per pound of aluminum

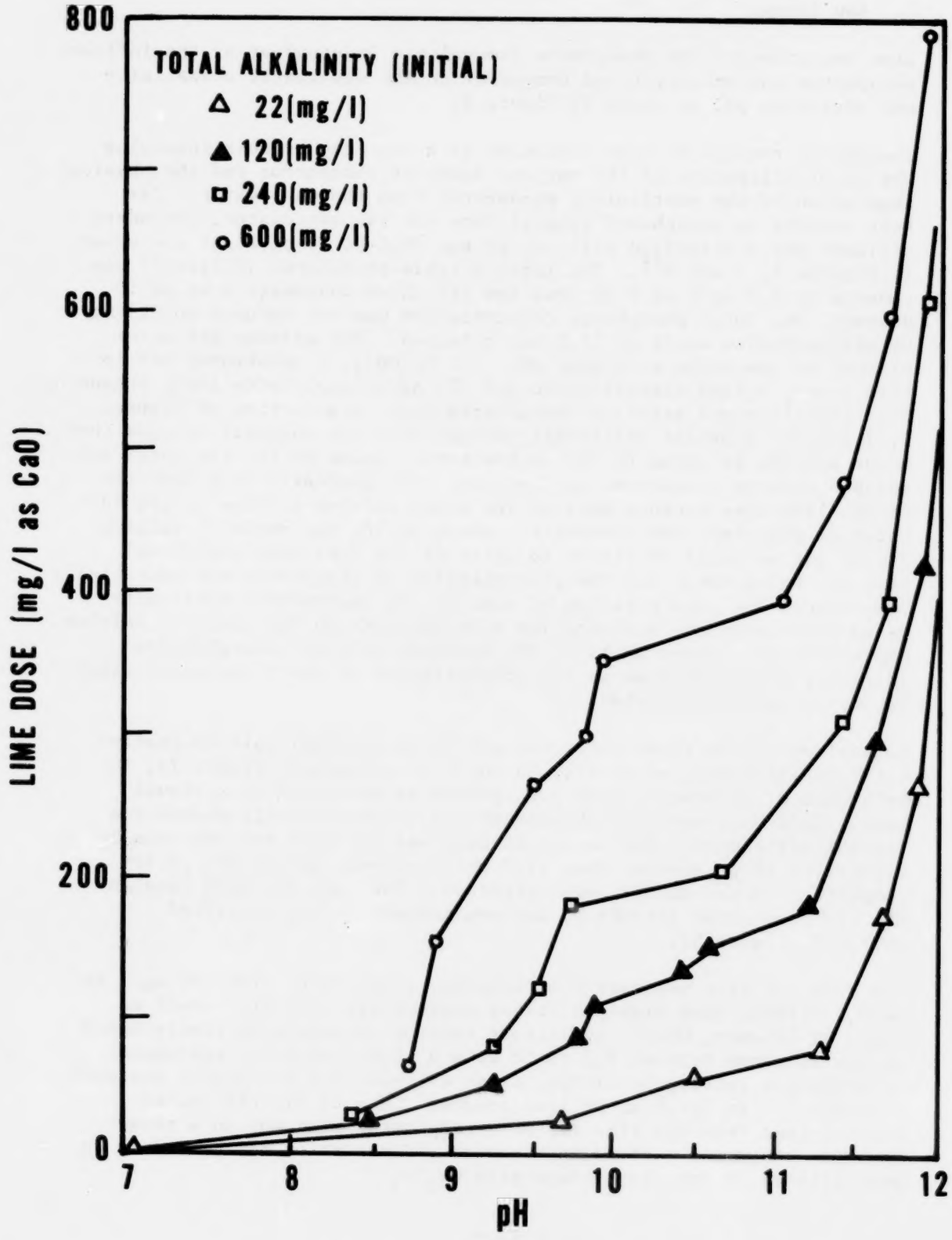


FIGURE 3
LIME REQIREMENTS AS A FUNCTION OF pH AND WASTEWATER ALKALINITY

1. Raw Sewage

Lime requirements for phosphorus removal are independent of the influent phosphorus concentration and dependent on the wastewater alakalinity and operating pH, as shown in Figure 3.

Phosphorus removal by lime treatment is a two-step process involving the insolubilization of the various forms of phosphorus and the physical separation of the particulate phosphorus from the wastewater. Jar test results on phosphorus removal from the raw wastewater, secondary effluent and a nitrified effluent at the FWQA-DC Pilot Plant are shown in Figures 4, 6 and 8[21]. The total soluble phosphorus (filtered) was reduced to 0.3 mg/l as P or less for all three wastewaters at pH 10. However, the total phosphorus concentration was not reduced to 0.3 mg/l by sedimentation until pH 11.5 was attained. Two effects are accomplished by operation at higher pH: (1) $Mg(OH)_2$, a gelatinous precipitate forms, aiding clarification and (2) additional $CaCO_3$ forms enhancing floc stability and settling characteristics. Examination of Figures 5, 7 and 9[21] provides additional insight into the chemical changes that occur as lime is added to the wastewaters. Below pH 10, the total and soluble calcium concentrations increase only gradually as a function of the lime dose because part of the added calcium settles as precipitates of phosphate and carbonate. Above pH 10, the residual calcium (total and soluble) decreased in spite of the fact that additional lime was being added and the precipitation of phosphorus was essentially completed. The precipitation of most of the bicarbonate alkalinity as calcium carbonate accounts for this decrease in the residual calcium concentration. Above pH 11.5, the residual calcium concentration increases with lime dose as the precipitation of the bicarbonate alkalinity is nearly completed.

Comparison of the soluble calcium and total residual calcium concentrations indicates, especially in the D.C. secondary (Figure 7), the existence of an unsettleable precipitate as evidenced by a visual haze. This haze contains phosphorus and reduces overall phosphorus removal efficiency. The amount of haze was variable and was usually eliminated at pH greater than 11.5 which corresponds to the pH for completion of the $Mg(OH)_2$ precipitation. The haze was much less in the raw wastewater (Figure 5) and nonexistent in the nitrified effluent (Figure 9).

The behavior of a wastewater of moderate alakalinity (100-150 mg/l as $CaCO_3$) differs from highly alkaline wastewaters (350 mg/l) such as found at Lebanon, Ohio. Sufficient calcium carbonate is precipitated in the pH range between 9.5 to 10 with a highly alkaline wastewater to produce a settleable sludge, clear effluent and filterable residual turbidity[7]. In the high pH lime process (pH = 11.5), the excess calcium ions from the lime may be precipitated with CO_2 in a recarbonation basin and settled in a second sedimentation basin, or may be precipitated in the first stage with Na_2CO_3.

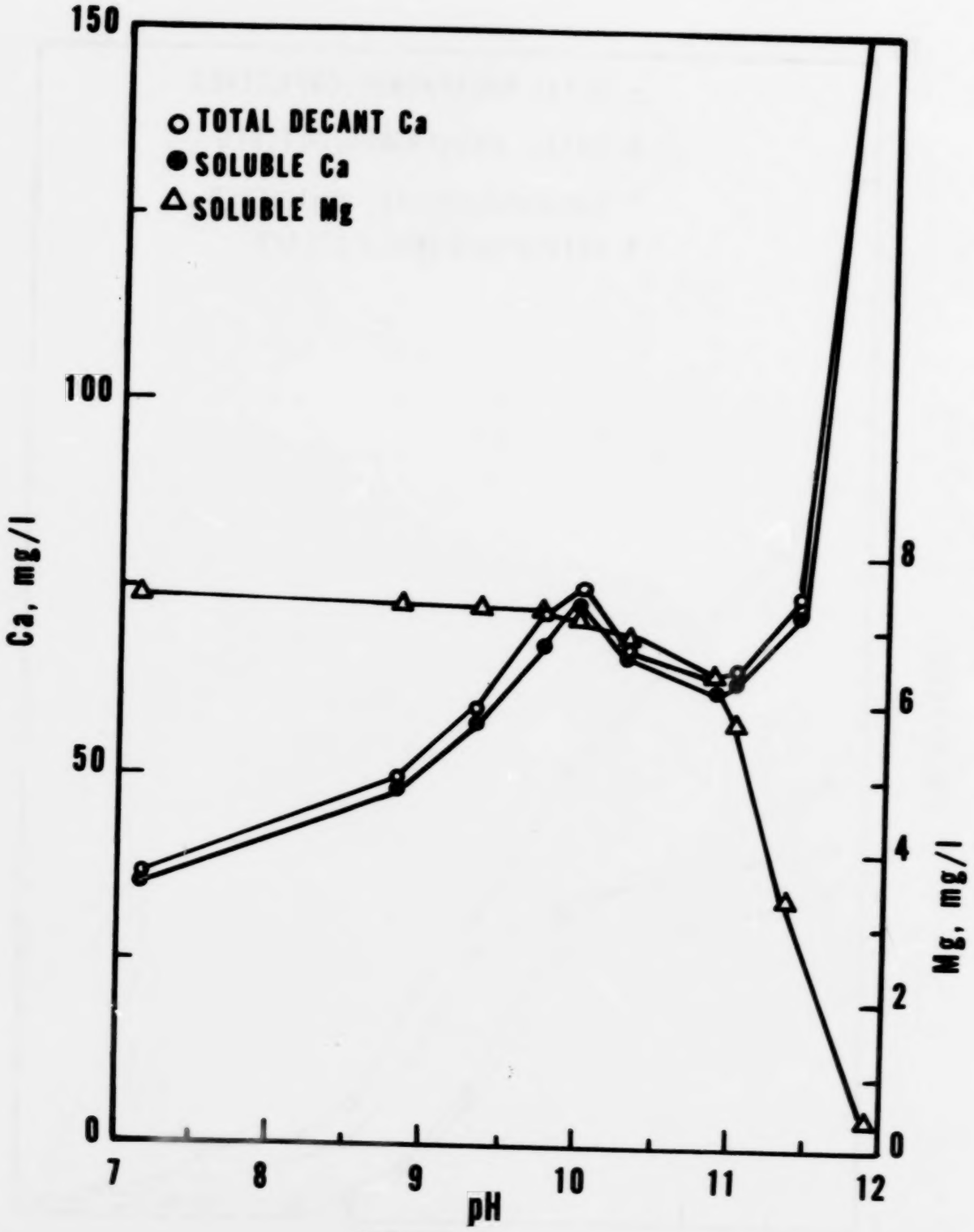


FIGURE 5

CALCIUM AND MAGNESIUM CONCENTRATIONS IN LIME TREATED D.C. RAW WASTEWATER AS A FUNCTION OF pH

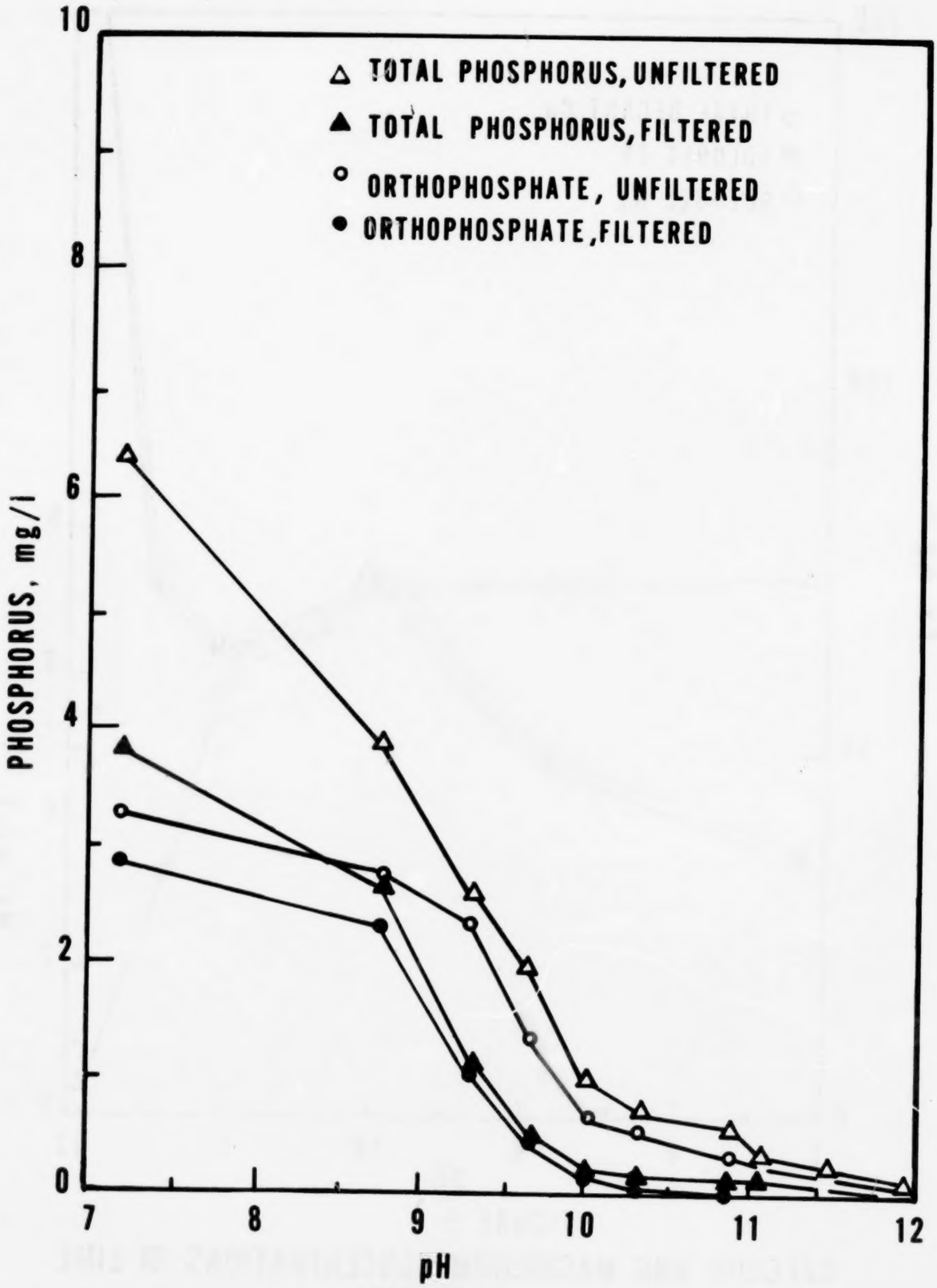


FIGURE 4
RESIDUAL PHOSPHORUS IN LIME TREATED D.C.
RAW WASTEWATER AS A FUNCTION OF pH

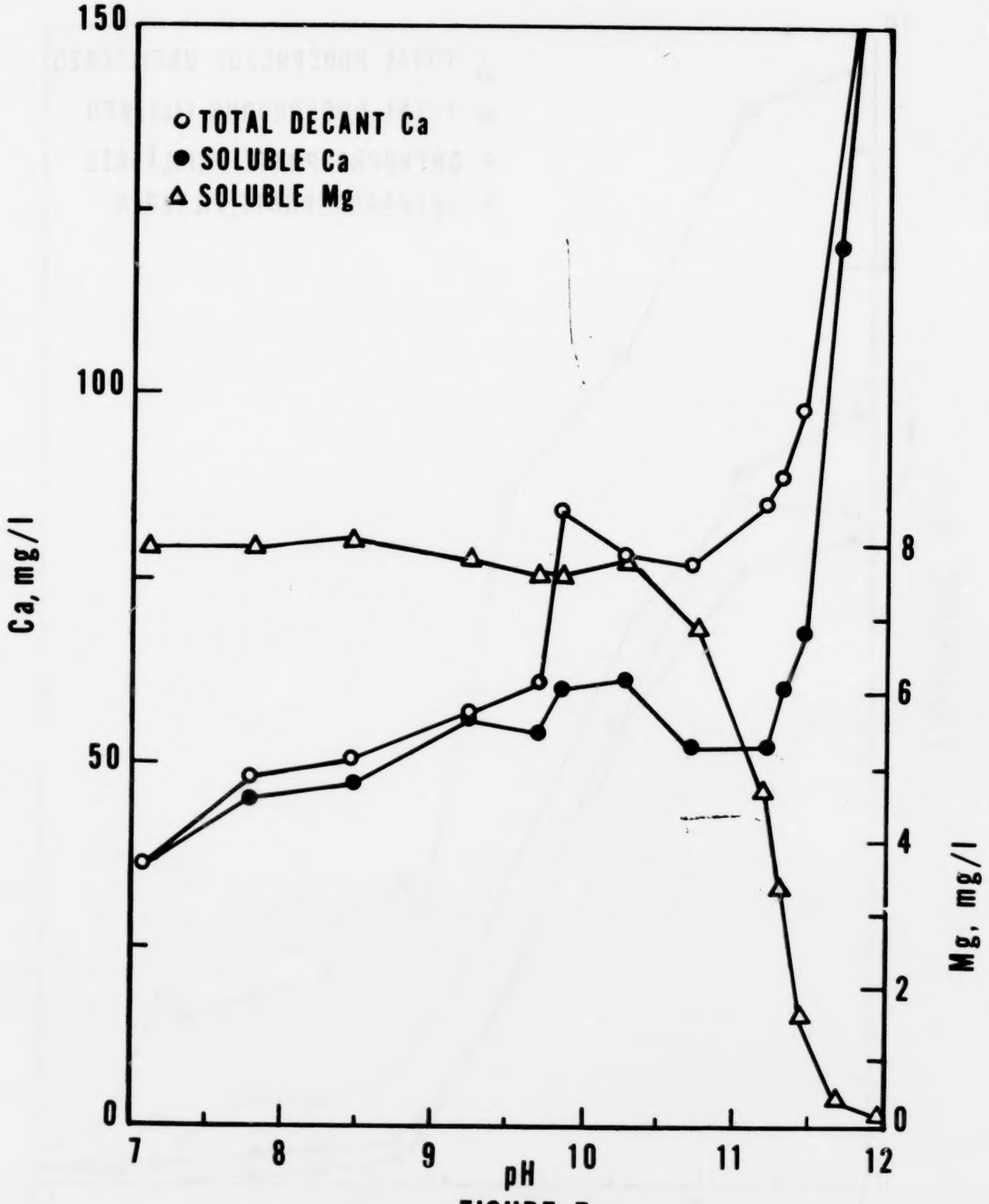


FIGURE 7

CALCIUM AND MAGNESIUM CONCENTRATIONS IN LIME TREATED D.C. SECONDARY EFFLUENT AS A FUNCTION OF pH

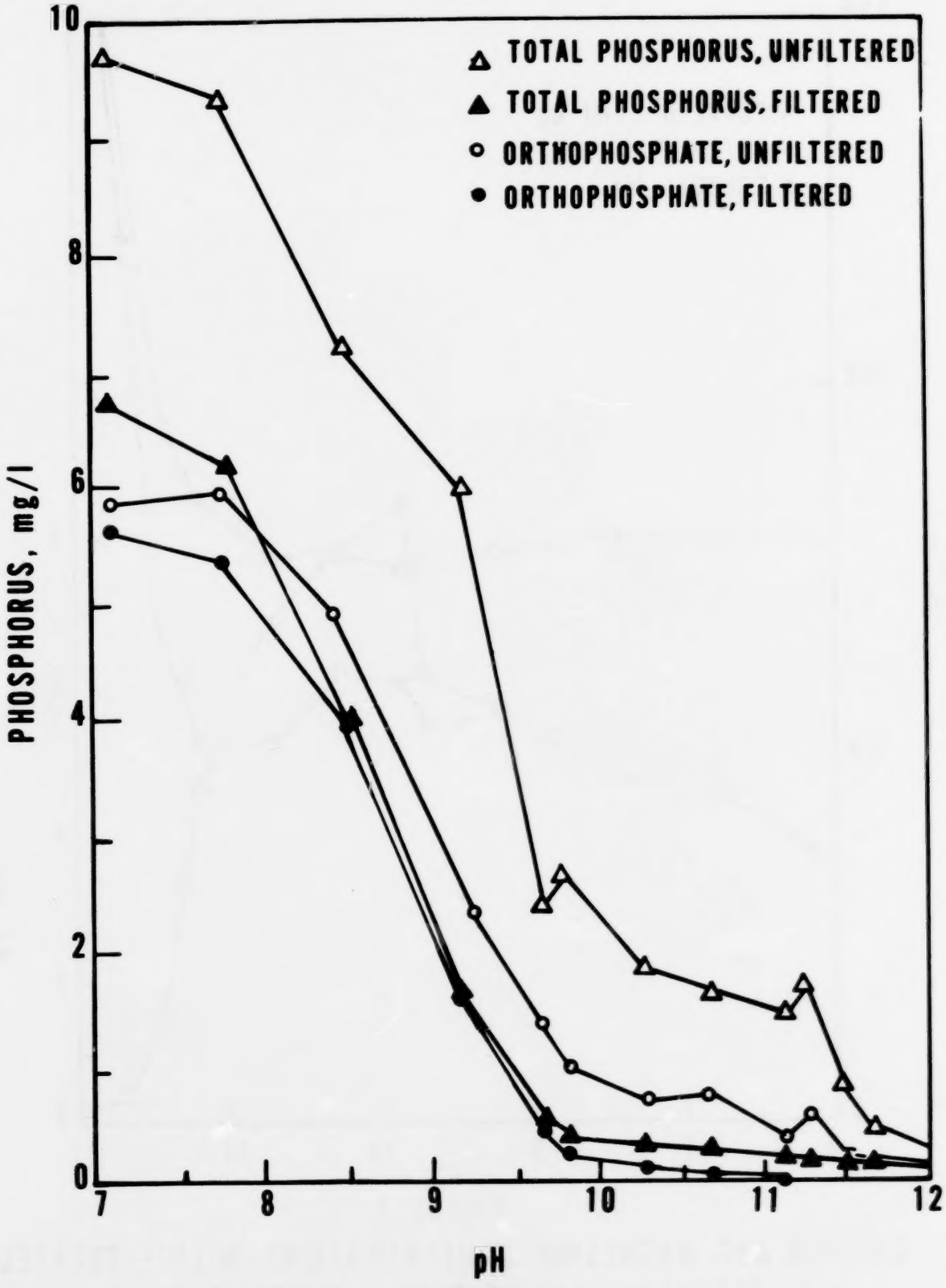


FIGURE 6
RESIDUAL PHOSPHORUS IN LIME TREATED D.C. SECONDARY EFFLUENT AS A FUNCTION OF pH

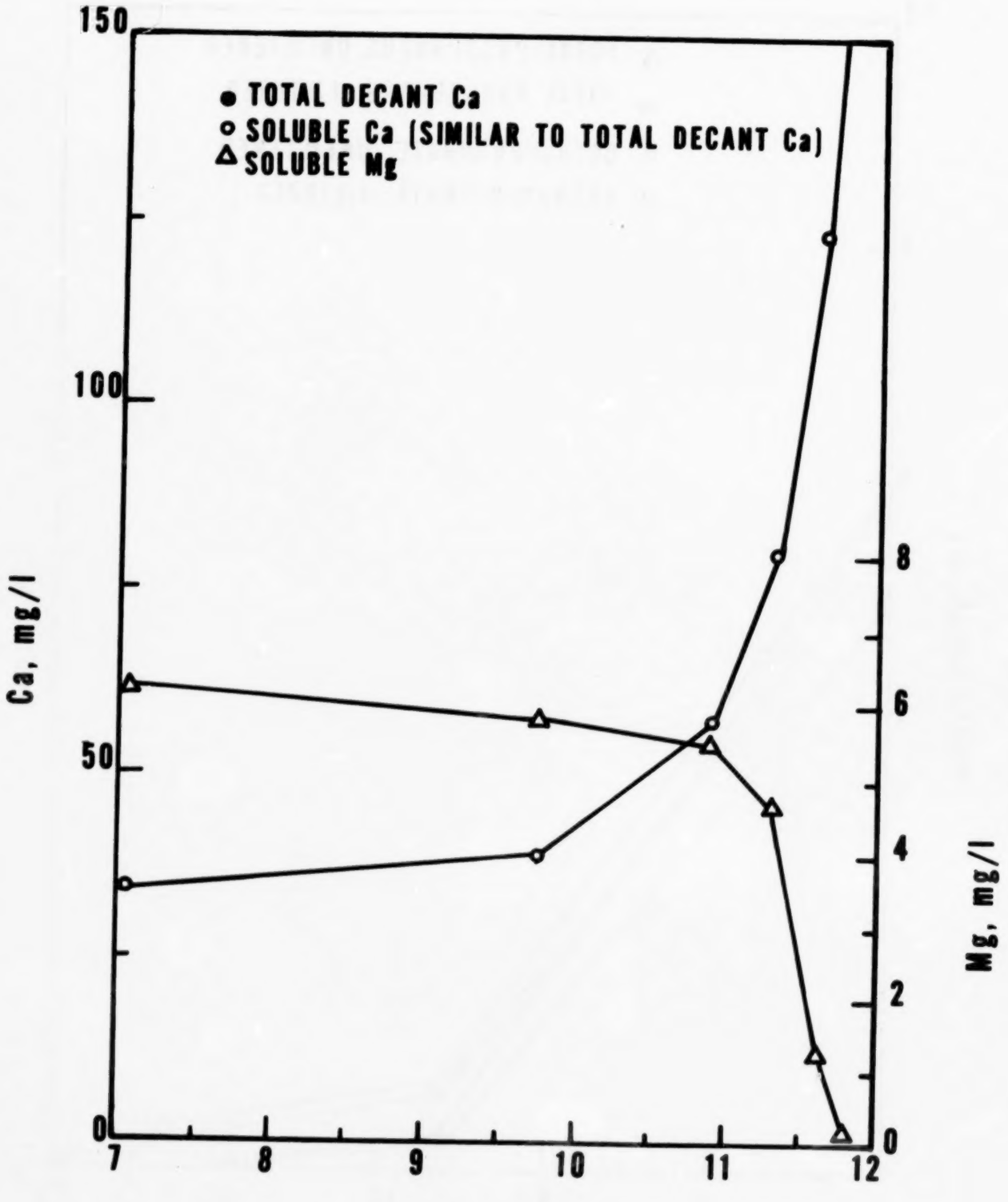


FIGURE 9
CALCIUM AND MAGNESIUM CONCENTRATIONS IN LIME TREATED NITRIFIED EFFLUENT AS A FUNCTION OF pH

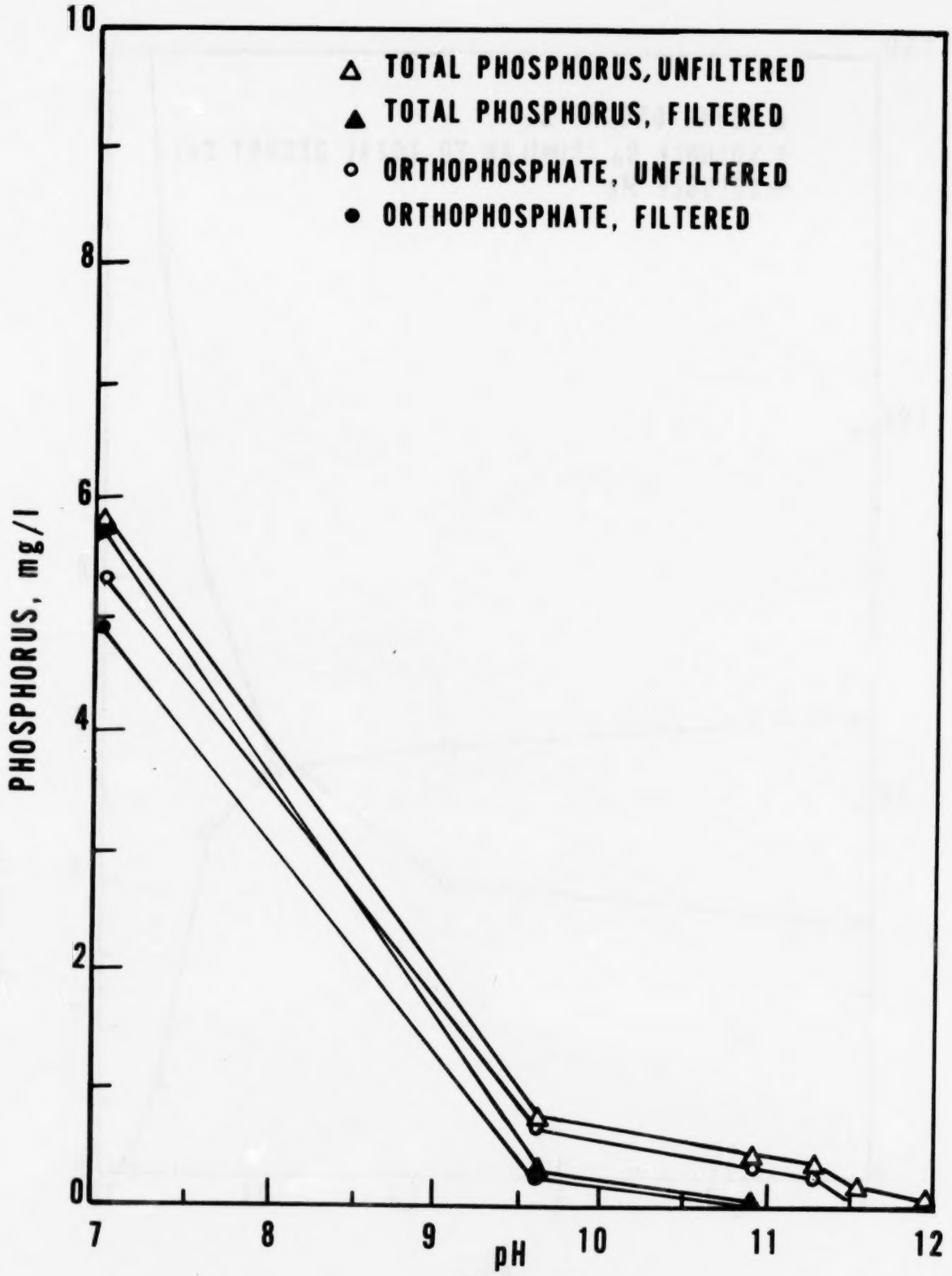


FIGURE 8
RESIDUAL PHOSPHORUS IN
LIME TREATED NITRIFIED EFFLUENT AS A FUNCTION OF pH

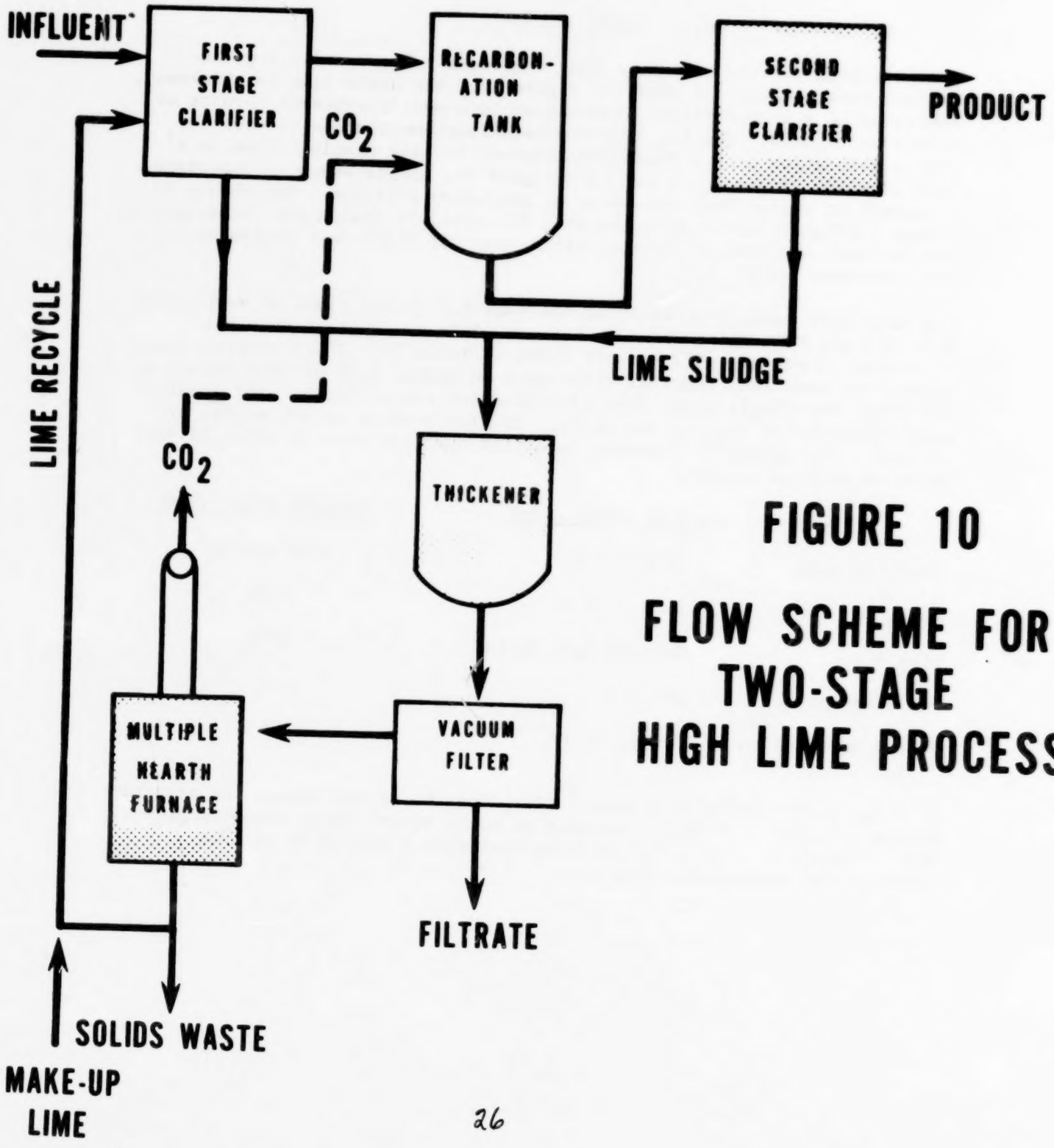


FIGURE 10

FLOW SCHEME FOR TWO-STAGE HIGH LIME PROCESS

The reactions for these alternatives are as follows:

$$Ca^{++} + 2\ OH^{-} + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$Ca^{++} + 2\ Na^{+} + CO_3^{=} \longrightarrow CaCO_3 + 2\ Na^{+}$$

A flow scheme for the two-stage lime treatment process utilizing intermediate recarbonation is shown in Figure 10. The waste lime is thickened, dewatered on a vacuum filter, recalcined in a multiple-hearth furnace at 1850°F and reused. The CO_2 from the recalcination furnace is used for the recarbonation step. Phosphorus removal by lime precipitation is a very flexible process. It can be designed for single-stage or two-stage treatment of either raw wastewater or secondary effluent. The choice of design configuration is governed by: (1) residual phosphorus requirements, (2) influent wastewater characteristics and (3) other unit processes in the treatment train.

The excellent results obtained at the FWQA-D.C. Pilot Plant at Washington, D.C. and the FWQA Pilot Plant at Lebanon, Ohio on physical-chemical treatment of primary effluent are shown in Table 14. These studies demonstrate the excellent removals attainable on either soft or hard waters by two-stage and single-stage lime clarification respectively. The studies were conducted on primary effluents. Similar studies on raw sewage are planned. The operating criteria in effect when the data in Table 14 was obtained were as follows:

	FWQA-DC PILOT PLANT	LEBANON PILOT PLANT
Overflow rate	1100 gpd/ft^2	1400 gpd/ft^2
1st stage pH	11.8 - 12.0	9.5
Lime dose	350-400 mg/l as CaO	250
2nd stage pH	10-10.5	-
Ferric addition to 2nd stage	5 mg/l as Fe^{+++}	-

A 10-mgd plant employing chemical clarification of raw sewage and granular carbon adsorption is being designed at Rocky River, Ohio. Construction and operation of this plant is being partially financed by an FWQA Research and Development Grant.

2. Tertiary Treatment

Single-stage and two-stage lime clarification can be applied as tertiary treatment processes. A notable example of two-stage tertiary lime treatment is the 7.5 mgd facility at Lake Tahoe. Phosphorus removal achieved by tertiary lime clarification is comparable to the results previously reported for primary effluent.

Lime requirements for the treatment of raw wastewater or secondary effluent at the same raw water source will differ depending on the type of secondary treatment. Conventional activated sludge can be expected to increase the lime requirements because of the CO_2 generated. Nitrification can be expected to consume alkalinity and lower the lime requirement.

Cost Estimates

The cost of single-stage lime clarification, without recarbonation or post filtration, for various sized plants are shown in Table 15. A lime requirement of 300 mg/1 as $Ca(OH)_2$ was assumed. Debt service charges were based on 4 1/2% for 25 years. Two other assumptions made for these cost estimates are that the cost of recalcining lime is equivalent to the cost of buying fresh lime and the cost saving associated with recalcining lime sludge is the cost of sludge disposal. The biggest cost associated with lime clarification for the larger plants is the cost of the lime. The cost of two-stage lime clarification exclusive of chemicals is shown in Figure 11.[20] The cost of recalcination and make-up lime is shown in Figure 12.[20] Plants smaller than about 10 mgd will use all new lime; larger plants will use recalcined plus make-up lime.

TABLE 15. Total Cost of Phosphate Removal for Single-Stage Lime Clarification[20]

	CENTS PER 1,000 GALLONS			
SIZE OF PLANT	1 mgd	10 mgd	100 mgd	250 mgd
Capital amortization	1.25	1.12	.84	.77
Land amortization	.12	.12	.12	.12
Operating and maintenance	2.30	.79	.50	.47
Cost of chemicals				
Lime	1.75	1.75	1.75	1.75
Cost of sludge disposal by hauling to land fill (25-mile one-way trip)	.67	.67	.67	.67
TOTAL	6.09	4.45	3.88	3.78
Savings if lime can be reclaimed	-.67	-.67	-.67	-.67
TOTAL (with recalcining)	5.42	3.78	3.21	3.11

TABLE 14. Results of Treatment by Lime Clarification, Filtration and Carbon Adsorption of Primary Effluent at Washington, D.C.[13] (I) and Lebanon, Ohio[24] (II)

	Two-Stage Lime Clarification - Low Alkaline Wastewater(I)		Single-Stage Lime Clarification - High Alkaline Wastewater(II)*	
	mg/l	% Removal	mg/l	% Removal
Primary Effluent				
Phosphorus, P	10.4		8.8	
TOC	78.4		76	
BOD	139		76	
COD	265		192	
S.S.	-		85	
Turbidity (J.T.U.)			55	
Lime Clarified Effluent				
Phosphorus, P	0.5	94.8		
TOC	27.1	65.2		
BOD	42.0	69.7		
COD	86	67.6		
S.S.	14.8			
Filtered Effluent				
Phosphorus	0.39	96.2	< 1	> 89
TOC	22.6	69.9	26	52.3
BOD	28	80.0	25	67.2
COD	66	75.0	67	65.0
S.S.	-		10	
Turbidity (J.T.U.)			2	
Carbon Effluent				
Phosphorus	-		< 1	> 89
TOC	6.5	90.6	10	87
BOD	4	97	10	87
COD	11	95.8	27	86
S.S.	-		1	
Turbidity (J.T.U.)			1	

* All analyses run by Standard Methods 12th Edition

Single-stage low pH lime clarification followed by activated sludge treatment has been suggested as a viable treatment technique to achieve 85% phosphorus removal. This combination of unit processes has been called the PEP Process and is being marketed by Dorr-Oliver, Inc.**

Rochester, New York is presently planning a 100 mgd plant incorporating lime clarification followed by activated sludge treatment.

** Trademark of Dorr-Oliver, Inc., Stamford, Connecticut (Use of trade name does not constitute an endorsement or recommendation by the Federal Government of the item or product mentioned.)

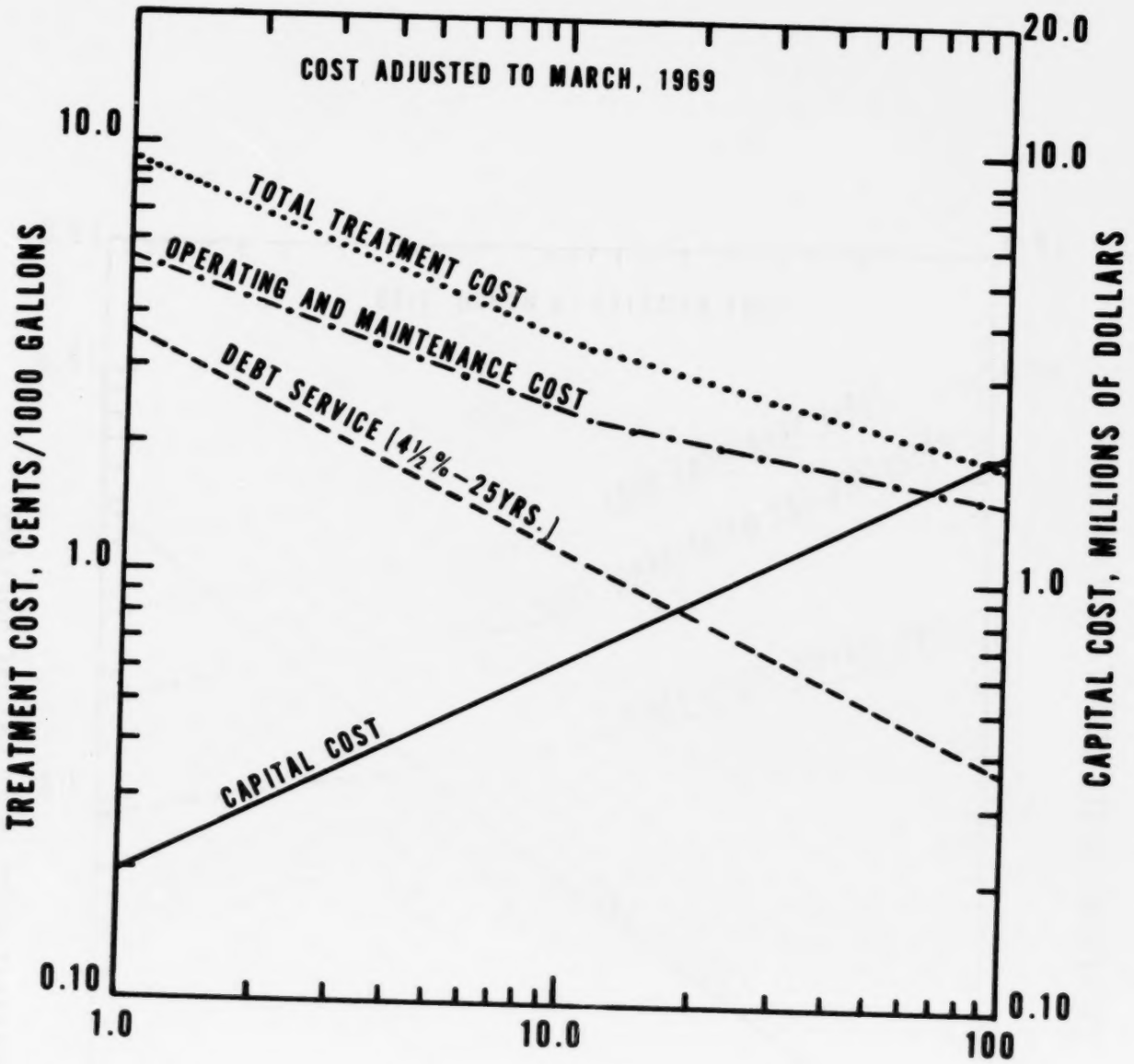


FIGURE 12

COST OF SUPPLYING LIME FOR LIME CLARIFICATION PROCESS*

*PLANTS LESS THAN ABOUT 10 MGD USE ALL NEW LIME;
LARGER PLANTS USE RECALCINED PLUS MAKE UP LIME

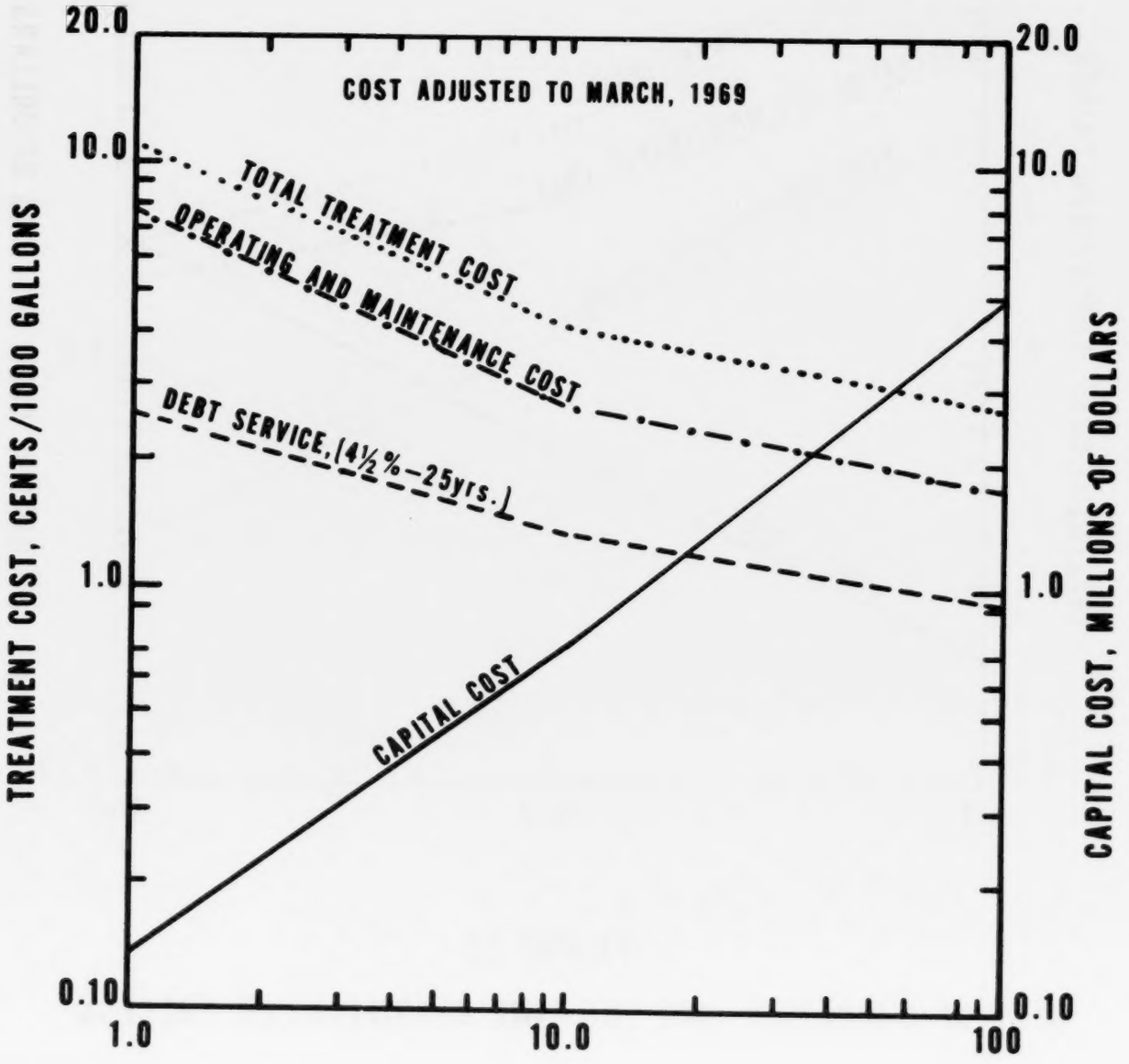


FIGURE 11
COST OF TWO STAGE LIME CLARIFICATION TREATMENT
EXCLUSIVE OF CHEMICALS

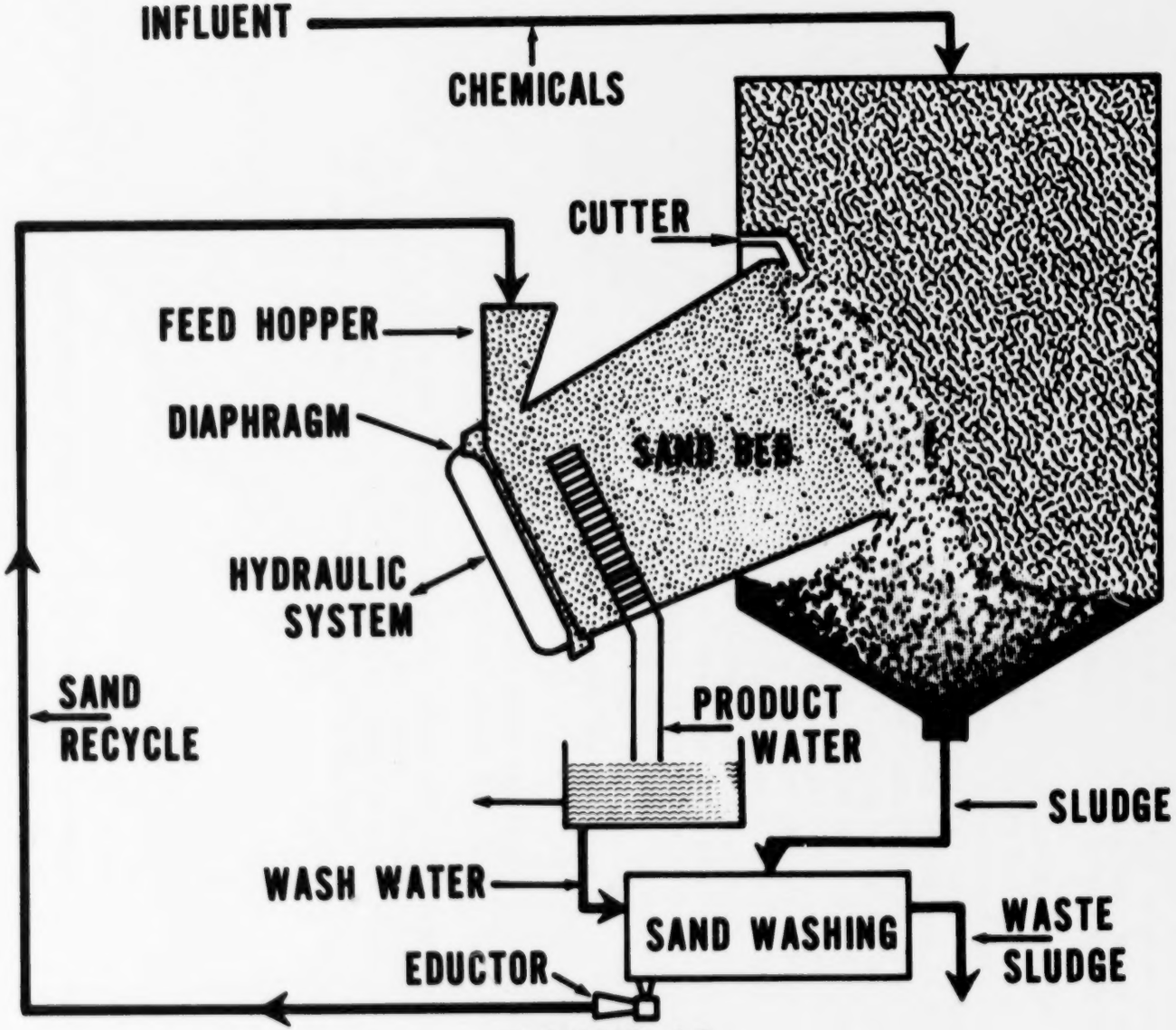


FIGURE 13

SCHEMATIC ARRANGEMENT OF MOVING BED FILTER

III. MOVING BED FILTRATION OF ALUM TREATED WASTEWATER

As mentioned earlier, phosphorus removal is a two-step process involving insolubilization and solids separation. An alternative to chemical treatment and settling is chemical precipitation and filtration. Either a coarse media upflow filter or a multi-media downflow filter may be used, but both have serious operational limitations. These include: (1) a limited ability to handle the wide fluctuations in solids load, and (2) potential plugging from biological growths which may occur in a fixed bed in the presence of high organic concentrations.

A new filter technology for wastewater involves the concept of a moving bed. A Moving Bed Filter (MBF) developed by Johns-Manville Products Corporation* has been operated under test conditions for over a year, including limited testing on the treatment of raw sewage. A schematic diagram of the MBF is shown in Figure 13. This unit is basically a sand filter with optional chemical treatment. Particulate matter is removed as the water passes through the sand bed. As the filter surface becomes clogged, the filter media is moved forward by means of a mechanical diaphragm. The clogged filter surface is hydraulically or mechanically removed thereby exposing a clean filter surface. The sand and accumulated sludge is washed and separated. The sand is returned to the base of the filter. The sand moves countercurrent to the water being filtered. The unit does not have to be taken off stream for backwashing. In theory, 1% of the filter is being backwashed 100% of the time compared to the conventional practice of backwashing 100% of the filter 1% of the time. External and more thorough cleaning of the filter media may prove to be an important factor in minimizing problems associated with slime growths.

Results from an 8-gpm MBF unit treating raw wastewater at Bernard's Township, New Jersey are shown in Table 16[12].

The Moving Bed Filter is being designed for plant capacities up to 5 mgd. Moving bed filtration of raw wastewater followed by granular carbon adsorption would appear to be an efficient alternative physical-chemical treatment combination; particularly, where land is scarce or expensive.

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* Mention of a commercial product does not imply endorsement by the FWQA or the U. S. Government.

TABLE 17. Results of Alum Coagulation and Moving Bed Filtration of Unsettled Trickling Filter Effluent[12]

Constitutent	Unsettled Trickling Filter Effluent mg/l	MBF Effluent mg/l	% Removal
BOD	40	5	87.3
Phosphorus as P:			
Total	19.1	0.84	96.1
Ortho	12.9	0.43	97.0
Filterable	15.5	0.50	97.1
Suspended Solids	96	7	92.8
Turbidity	41	2.9	93.0

Cost Estimates

The capital costs of a 1-mgd Moving Bed Filter are estimated to be $190,000. Erection costs including influent pumps, electrical and plumbing are an additional $90,000. The total operating costs including amortization of capital is estimated to be $0.13/1,000 gal.

Sludge disposal costs with a rotary precoat vacuum filter are estimated at an additional $0.02 to $0.03/1,000 gal. based on experience with water treatment plant sludges.[17]

TABLE 16. Results of Alum Coagulation and Moving Bed Filtration Treatment of Raw Wastewater at the Bernard's Township Plant

Constituent	Raw Wastewater Concentration mg/l	MBF Effluent Concentration mg/l	% Removal
BOD	115	19	83.5
Phosphorus as P:			
Total	21.5	2.2	90.0
Ortho	13.2	0.6	95.5
Filterable	18.6	0.8	95.5
Suspended Solids	156	27	83.0
Turbidity, JTU	119	16	86.5
Test Conditions:			
Flow Rate	2.5 gpm/ft^2		
Alum Dose	200 gpm/l		
Polymer	.5-.65 mg/l		

The primary application for which the Moving Bed Filter was designed is the filtration of unsettled trickling filter effluent. Results of the MBF unit in this application are shown in Table 17.[12]

Test conditions for the filtration of unsettled trickling filter effluent were identical to the test conditions for the filtration of raw wastewater.

A 2-mgd Moving Bed Filter facility at the Borough of Manville Plant for the treatment of unsettled trickling filter effluent is currently under construction. This project is being partially funded through an FWQA Research and Development Grant.

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SUMMARY AND CONCLUSIONS

There are several alternative methods available for the removal of phosphorus including biological uptake, chemical precipitation of the soluble phosphorus and either settling or filtration of the particulate phosphorus.

Based on today's technology, chemical precipitation is the most practical method of phosphorus removal. There are numerous chemical systems available which can be applied to raw sewage, primary effluent or secondary effluent. The choice of chemical and point of chemical addition depend to a great extent upon the size of plant, phosphorus discharge standard, influent wastewater characteristics and other processes utilized in the treatment train.

Phosphorus removal costs range from $0.13/1,000 gal. for two-stage lime treatment of raw sewage to attain 97% removal at 1-mgd to a potential low of $0.015/1,000 gal. for the use of waste pickle liquor in the primary to achieve 80% phosphorus removal.

In the process of removing phosphorus, several other benefits including better solids and BOD removal occur. As with all pollution control, the benefits must be weighed against the costs.

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10 Author(s)

Convery, John J.

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27 Abstract

Technology is available to remove the nutrient phosphorus from municipal wastewaters. This paper summarizes the alternative methods for both biological and physical-chemical treatment. The information should be helpful in providing perspective to municipal officials, engineers and treatment plant operators contemplating incorporation of nutrient control measures into their treatment facilities. Process selection will depend on specific wastewater characteristics, existing facilities, required effluent quality, and economic considerations.

Processes discussed include conventional biological treatment, digester supernatant treatment, modified biological treatment, chemical addition in primary, secondary and tertiary stages of treatment, and moving bed filtration.

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